

DECLARATION

I, Ryuichi YAMADA, a Japanese Patent Attorney registered No. 7898 having my Business Office at Hasegawa Bldg., 4F, 7-7 Toranomom 3-chome, Minato-ku, Tokyo, Japan, solemnly and sincerely declare:

That I have a thorough knowledge of Japanese and English languages; and

That the attached pages contain a correct translation into English of the specification of the following Japanese Application:

APPLICATION
NUMBER

DATE OF
APPLICATION

106380/2000(Pat.)

7/APR/2000

Applicant(s)

CANON KABUSHIKI KAISHA

Signed this 14~~th~~ day of July, 2004.


Ryuichi YAMADA

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true
copy of the following application as filed with this Office.

<u>APPLICATION NUMBER</u>	<u>DATE OF APPLICATION</u>
106380/2000(Pat.)	7/APR/2000

Applicant(s)
CANON KABUSHIKI KAISHA

27/APR/2001

Director-General,
Patent Office : KOZO OIKAWA (Seal)

Certificate No. 3035613/2001

<FILE NO.> 4132011

<DOCUMENT> PATENT APPLICATION

<FILE NO.> 4132011

<FILING DATE> 7/APR/2000

<DIRECTED TO> The Director General of the Patent Office

<INTERNATIONAL CLASSIFICATION> C09K 19/00

<TITLE OF THE INVENTION> ELECTROCONDUCTIVE LIQUID CRYSTAL DEVICE

<NUMBER OF CLAIMS> 6

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<PREPAY REGISTRATION NO.> 015417
<AMOUNT> 21000

<ARTICLES PRESENTED>

<ARTICLE> Specification 1
<ARTICLE> Drawing(s) 1
<ARTICLE> Abstract 1
<GENERAL POWER NO.> 9703886

<REQUEST FOR PROOF> YES

[Document]

Specification

[Title of the Invention]

Electroconductive Liquid Crystal Device

[Claims]

1. A conductive liquid crystal device,
comprising:

a pair of oppositely disposed electrodes;
a liquid crystalline organic layer disposed
between the oppositely disposed electrodes; and
wherein the liquid crystalline organic layer
is provided with plural regions having mutually
different electroconductivities.

2. A conductive liquid crystal device according
to Claim 1, wherein the plural regions having mutually
different electroconductivities of said liquid
crystalline organic layer has been formed by
controlling the alignment states of liquid crystal
molecules.

3. A conductive liquid crystal device according
to Claim 2, wherein said local alignment state change
of liquid crystal molecules of said liquid crystalline
organic layer has been formed by laser light

irradiation of said liquid crystalline organic layer.

4. A conductive liquid crystal device according to Claim 2, wherein said local alignment state change of liquid crystal molecules of said liquid crystalline organic layer has been formed by voltage application to said liquid crystalline organic layer.

5. A conductive liquid crystal device,
comprising:

- a pair of oppositely disposed electrodes;
- a liquid crystalline organic layer disposed between the oppositely disposed electrodes; and
- wherein the liquid crystalline organic layer is provided with plural regions having mutually different electroconductivities, and said local alignment state change of liquid crystal molecules of said liquid crystalline organic layer is displayed by transforming said conductive liquid crystal device from said local alignment state change into the current change of said liquid crystalline organic layer.

6. A conductive liquid crystal device,
comprising:

- a pair of oppositely disposed electrodes;
- a liquid crystalline organic layer disposed

between the oppositely disposed electrodes; and wherein at least one of organic layers comprises a liquid crystalline organic layer, said liquid crystalline organic layer is provided with plural regions having mutually different electroconductivities, and said mutually different electroconductivities of liquid crystal molecules of said liquid crystalline organic layer is displayed by transforming said conductive liquid crystal device from said local alignment state change into the current change of said liquid crystalline organic layer.

[Detailed Description of the Invention]

[Field]

The present invention relates to an electroconductive liquid crystal device, more particularly, it relates to an organic electroluminescence device (hereinafter, the term "electroluminescence" being sometimes breviated as "EL" according to common usage in the field) using the electroconductive liquid crystal device.

[Prior Art]

As for the organic EL device, carrier injection-type EL devices utilizing organic solids, such as anthracene single crystal, were studied in detail in years of 1960's. These devices were of a

single layer-type, but thereafter Tang, et al proposed a lamination-type organic EL device comprising a luminescence layer and a hole transporting layer between a hole injecting electrode and an electron injecting electrode. The luminescence mechanism in these injection-type EL devices commonly includes stages of (1) electron injection from a cathode and hole injection from an anode, (2) movement of electrons and holes within a solid, (3) re-combination of electrons and holes, and (4) luminescence from the resultant single term excitons.

A representative example of the lamination-type EL device may have a structure including an ITO film as a anode formed on a glass substrate, a ca. 50 nm-thick layer formed thereon of TPD (N,N'-diphenyl-N,N'-di(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine), a ca. 50 nm-thick layer thereon of Alq3 (tris(8-quinolinolato)-aluminum), and further a vacuum deposition layer of Al-Li alloy as a cathode. By setting the work function of the ITO used as the anode at 4.4 - 5.0 eV, the hole injection to TPD is made easier, and the cathode is composed of a metal which has as small a work function as possible and also is stable. Examples of the cathode metal may include Al-Li alloy as mentioned above and also Mg-Ag alloy. By the above organization, green luminescence may be obtained by applying a DC voltage of 5 - 10 volts.

An example using a conductive liquid crystal as a carrier transporting layer is also known. For example, D. Adam et al (Nature, Vol. 371, p. 141-) have reported that a long-chain triphenylene compound as a discotic liquid crystal material exhibited a mobility of $10^{-3} - 10^{-2} \text{ cm}^2/\text{V}\cdot\text{sec}$ in its liquid crystal phase (Dh phase) and a mobility of $10^{-1} \text{ cm}^2/\text{V}\cdot\text{sec}$ in its mesophase (an intermediate phase, not a liquid crystal phase). Also, as for a bar-shaped liquid crystal, Junichi Hanna (Ohyou Butsuri (Applied Physics), Vol. 68, No. 1, p. 26-) has reported that a phenylnaphthalene compound exhibited a mobility of $10^{-3} \text{ cm}^2/\text{V}\cdot\text{sec}$ or higher in its smectic B phase.

As a trial for using such a liquid crystal for electroluminescence (EL), INGAH STAPFF et al. (Liquid Crystals, Vol. 23, No. 4, pp. 613-617) have reported an organic EL device using a triphenylene-type discotic liquid crystal. Other reports are found in POLYMERS FOR ADVANCES TECHNOLOGIES, Vol. 9, pp. 463-460 (1998), and ADVANCED MATERIALS (1997), Vol. 9, No. 1, p. 48-.

[Problems to be Solved]

Convention organic EL devices have involved several problems attributable to the use of a low-molecular weight compound in a crystal state. A first problem is that the efficiency of injection of

electrons or holes from electrodes of ITO, etc., to the organic layers is low. This is because minute grain boundary in a crystal state of organic molecules functions as a carrier conduction barrier. Accordingly, organic molecules in an amorphous state are generally used though it incurs a low carrier injection efficiency. This however has provided a major cause why an organic EL device cannot ensure a large current.

An organic material used in an organic EL device has an electronic structure providing a large energy gap of ca. 3 eV or larger, thermal excitation-type free electrons are not present in a conduction band, a drive current (spatial charge restriction current) is principally supplied by injected carriers from the electrodes, so that a low carrier injection efficiency from the electrodes has been a serious problem. As the injection efficiency is low, a large voltage has to be applied in order to ensure a drive current, and the device layer thickness has to be lowered. These factors have caused difficulties, such as a short circuit between the electrodes and an increase in capacitive load.

As a second problem, an organic EL device is liable to be affected by invaded moisture to cause deterioration of luminescence performance and drive performance, thus showing poor durability. In an

ordinary organic EL device, the organic layers are disposed in lamination and then the cathode is formed thereon by vapor deposition of a metal film. In this instance, a metal species having a small work function suitable for the cathode is susceptible of oxidation and has a low durability. Even in case of forming a protective film thereon by sputtering, the organic layers are liable to be degraded if the forming temperature is high (with an ordinary limit of 100 °C), and the destruction of the device structure due to the film stress is also problematic.

On the other hand, as a problem accompanying the use of a conductive liquid crystal for constituting a carrier transporting layer, it is difficult to align a high order liquid crystal layer. As a high order conductivity can be attained by a regular stacking of π -electron conjugated planes of liquid crystal molecules, the degree of alignment thereof directly affects the conductivity of the resultant conductive liquid crystal layer. In the case of a poor alignment characteristic, trap sites for conduction of electrons and holes can be formed in the liquid crystal layer, so that electroconductivity can be lost at all in some cases.

The present invention was made in consideration of the above described technical problems. Accordingly, it is a principal object of

the present invention to provide a conductive liquid crystal device which is produced by forming a conductive liquid crystalline organic layer between a pair of oppositely disposed electrodes, and controlling an alignment state of the conductive liquid crystalline organic layer locally or entirely to form regions of different electroconductivities, and a memory characteristic, thereby causing luminescence exhibiting different luminances at an identical drive voltage.

[Means for Solving the Problems]

In accordance with a first aspect of the present invention, there is provided a conductive liquid crystal device, comprising: a pair of oppositely disposed electrodes; a liquid crystalline organic layer disposed between the oppositely disposed electrodes; and wherein the liquid crystalline organic layer is provided with plural regions having mutually different electroconductivities.

In a conductive liquid crystal device according to the present invention, it is preferable that the plural regions having mutually different electroconductivities of the liquid crystalline organic layer has been produced by controlling the alignment states of liquid crystal molecules. In addition, it is preferable that the local alignment state change of liquid crystal molecules of the liquid

crystalline organic layer has been formed by laser light irradiation of the liquid crystalline organic layer. It is also preferable that the local alignment state change of liquid crystal molecules of the liquid crystalline organic layer has been formed by voltage application to the liquid crystalline organic layer.

In accordance with a further aspect of the present invention, there is provided a conductive liquid crystal device, comprising: a pair of oppositely disposed electrodes; a liquid crystalline organic layer disposed between the oppositely disposed electrodes; and wherein the liquid crystalline organic layer is provided with plural regions having mutually different electroconductivities, and the local alignment state change of liquid crystal molecules of the liquid crystalline organic layer is displayed by transforming the conductive liquid crystal device from the local alignment state change into the current change of the liquid crystalline organic layer.

In accordance with a further aspect of the present invention, there is provided a conductive liquid crystal device, comprising: a pair of oppositely disposed electrodes; a liquid crystalline organic layer disposed between the oppositely disposed electrodes; and wherein at least one of organic layers comprises a liquid crystalline organic layer, the liquid crystalline organic layer is provided with

plural regions having mutually different electroconductivities, and the mutually different electroconductivities of liquid crystal molecules of the liquid crystalline organic layer is displayed by transforming the conductive liquid crystal device from the local alignment state change into the current change of the liquid crystalline organic layer.

[Description of the Preferred Embodiments]

According to an embodiment, the conductive liquid crystal device of the present invention may be produced by forming a conductive liquid crystalline organic layer on an electrode, and controlling an alignment state of the conductive liquid crystalline organic layer locally or entirely to form regions of mutually different electroconductivities, leading to different luminances of luminescence when used as an organic EL device.

A high electric field on the order of 10 volts/100 nm has been required for the drive of an organic EL device because of (1) a low mobility of carriers (holes and electrons) through organic layers and (2) a low efficiency of injection of carriers into the organic layers from the electrodes. Organic materials used in organic EL devices have a broad band gap of ca. 3.0 eV, so that thermal excitation-type free electrons are not present in a conduction band (LUMO: lowest unoccupied molecular orbital), and

drive current is principally supplied by a tunnel current injected from the electrodes. The injection efficiency of the current is known to be remarkably affected not only by the work functions of the electrodes and a level gap between LUMO and HOMO (Highest Occupied Molecular Orbital) of the organic materials but also by the molecular alignment and structure of the organic materials. However, in order to attain a sufficient drive current by using ordinary organic compounds (such as TPD, α -NPD (bis[N-(1-naphthyl)-N-phenyl]benzidine), TAZ-01 (3-(4-biphenyl)-4-phenyl-5-(4-tert-butylphenyl)-1,2,4-triazole), Alq3, etc.) in ordinary EL devices, it has been necessary to apply a high electric field (on the order of 10 V/100 nm) across the organic layer-electrode boundaries. Further, as the mobility of the organic materials is on the order of 10^{-6} - 10^{-3} cm²/V.sec, it is also necessary to apply a high electric field in order to ensure a drive current. Some improvement to the above problem has been given by using a conductive liquid crystal for constituting a liquid crystalline charge injection layer as proposed by our research group. Japanese Laid-Open Patent Application Nos. HEI-11-255007 and HEI-11-273879. The use of a conductive liquid crystal for constituting a charge injection layer is effective because of the following reasons and functions.

On the other hand, in order to control the local alignment state of the conductive liquid crystalline organic layer, the conductive liquid crystalline organic layer is heated locally, and the local alignment state change is principally performed by controlling the conductive liquid crystalline layer in a phase transition thereof. Hereinafter, the functions thereof will be described.

The method for controlling the alignment state of the conductive liquid crystalline layer can alternatively be effected by a surface treatment of an electrode surface, such as local surface roughening the regions for not aligning the liquid crystal on the electrode surface.

(1) Some conductive liquid crystallines have a mobility exceeding 10^{-2} cm²/V.sec (D. Adam, et al; Nature Vol. 371, p. 141-).

(2) A conductive liquid crystal causes a phase transition at a higher temperature to assume a lower order liquid crystal phase, such as nematic phase or discotic disordered phase, thereby showing a good alignment characteristic to cause alignment of liquid crystal molecules over an electrode surface.

(3) Especially, a discotic liquid crystal generally has a structure including a core of, e.g., triphenylene, and side chains attached to the periphery of the core for developing mesomorphism

(liquid crystal property). The side chains generally exhibit poor wettability with a substrate of a metal or a metal oxide (such as ITO), so that in the liquid crystal state of the discotic liquid crystal, the core is aligned parallel to the electrode surface, whereby the π -electron resonance plane of the core is aligned parallel to the electrode surface, thereby facilitating carrier transfer with the electrode. Accordingly, it is possible to provide a higher injection efficiency than an ordinary organic compound in an amorphous state. This effect can also be expected for an ordinary bar-shaped liquid crystal having a molecular structure including a phenyl group or a naphthalene group having a π -electron resonance plane.

(4) The formation of a conductive liquid crystal layer as a carrier transporting layer by vacuum deposition is particularly effective. A liquid crystal film layer formed by vacuum deposition has a coarse molecular packing state, the re-alignment thereof by heating is very easy. This is particularly true with a liquid crystal film formed by vacuum deposition on a substrate at a temperature close to or below T_g (glass transition temperature) of the liquid crystal giving a stably coarse film structure.

(5) A high-order liquid crystal phase having a higher degree of order has a low fluidity; and the alignment thereof in the high-order liquid crystal

phase per se is difficult, whereas the alignment characteristic thereof can be improved if the liquid crystal layer is sandwiched between films having a power of aligning π -electron conjugated planes parallel thereto. Realignment by heating up to the isotropic phase is not desirable for device formation sometimes because of a strong dissolving power of the liquid crystal material in a liquid phase to other organic materials, but the dissolution problem is not encountered at a boundary with a metal film. In the case of sandwiching a liquid crystal with metal films, one of them is required to allow light-transmission. For example, in the case of using a gold film, the film may be formed as an island-like uneven film, but the alignment thereby of a liquid crystal can be improved than in the absence of such a gold film.

(6) A molecule exhibiting mesomorphism can re-organize molecular disposition at the electrode surface by re-aligning post treatment. This can facilitate the injection efficiency. The post treatment can exhibit a large effect even when it is performed by heating only to a liquid crystal phase temperature if it provides a lower viscosity. The heating to the isotropic temperature, while it is effective for the re-alignment, has to be suppressed to a temperature below the T_g of other organic materials used together therewith.

(7) At a boundary of a luminescence layer with a liquid crystal layer or an intermediate metal layer, it is effective to insert a protective layer comprising a material having a function of transporting a carrier of the same type.

The conductive liquid crystal device structure including a conductive liquid crystal layer having a locally different conductivity can be effectively used for constituting an organic EL device as described in detail below but also for constituting other functional devices, such as a photosensor, a photoconductor (electrophotographic photosensitive member), an organic semiconductor device (such as an organic TFT), a temperature sensor, and a space modulation device.

Figure 1 is a schematic sectional view of an embodiment of the conductive liquid crystal device according to the present invention. Referring to Figure 1, the conductive liquid crystal device includes a transparent substrate 1, and a transparent electrode (anode) 2, a liquid crystalline organic layer 3, a luminescence layer 5 and a metal electrode (cathode) 6 disposed in this order on the substrate 1, wherein the liquid crystalline organic layer 3 is provided with plural regions having mutually different electroconductivities including non-aligned liquid crystal regions 5a having a lower conductivity and

aligned liquid crystal regions 5b having a higher conductivity.

The liquid crystalline organic layer 3 comprises a liquid crystalline or mesomorphic compound having a liquid crystal phase at some temperature, inclusive of low-molecular weight (non-polymeric) conductive liquid crystals and polymeric conductive liquid crystals. The conductive liquid crystal may suitably have a π -electron resonance structure, which is generally given by an aromatic ring. Examples thereof may include: triphenylene ring, naphthalene ring and benzene ring, as representative, and also pyridine ring, pyrimidine ring, pyridazine ring, pyrazine ring, tropone ring, azulene ring, benzofuran ring, indole ring, indazole ring, benzothiazole ring, benzoxazole ring, benzimidazole ring, quinoline ring, isoquinoline ring, quinazoline ring, quinoxaline ring, phenanthrene ring and anthracene ring.

The conductive liquid crystal used in the present invention may preferably comprise a discotic liquid crystal or a smectic liquid crystal. A discotic liquid crystal may generally have a core structure which may be given by an aromatic ring as mentioned above for the π -electron resonance structure, as represented by triphenylene ring (or skeleton). Further examples thereof may include truxene skeleton, metal-phthalocyanine skeleton,

phthalocyanine skeleton, dibenzopyrene skeleton, metal-naphthalocyanine skeleton, dibenzopyrene skeleton, and hexabenzocoronene skeleton.

As for the electrode materials used in the present invention, examples of material constituting the anode 2 may include: indium oxide, tin oxide, Cd_2SnO_4 , zinc oxide, copper iodide, gold and platinum, in addition to ITO used in Examples described hereinafter. Examples of material constituting the cathode 6 may include: alkali metals, alkaline earth metals and alloys of these, inclusive of sodium, potassium, magnesium, lithium, sodium-potassium alloy, magnesium-indium alloy, magnesium-silver alloy, aluminum, aluminum-lithium alloy, aluminum-copper alloy, aluminum-copper-silicon alloy.

Further, examples of materials for the luminescence layer 5 may include: in addition to Alq3, BeBq (bis(benzoquinolinolato)beryllium), DTVB2 (4,4'-bis(2,2-di-p-tolylvinyl)biphenyl), $\text{Eu}(\text{DBM})_3(\text{Phen})$ (tris(1,3-diphenyl-1,3-propanediono)-monophenanthroline) $\text{Eu}(\text{III})$), and further, diphenyl-ethylene derivatives, triphenylamine derivatives, diaminocarbazole derivatives, bisstyryl derivatives, benzothiazole derivatives, benzoxazole derivatives, aromatic diamine derivatives, quinacridone compounds, perylene compounds, oxadiazole derivatives, coumarin compounds, anthraquinone derivatives, distyrylarylene

derivatives (DPVBi), and oligothiophene derivatives (BMA-3T).

Further, as mentioned above, a protective layer can be inserted adjacent to the liquid crystalline organic layer 3. The protective layer may preferably comprise a material having a large volume so as to exhibit little diffusivity into liquid crystalline materials used in the liquid crystalline organic layer 3. It is further preferred that the protective layer material does not have a liquid crystal phase of an order equivalent to or lower than that of a disordered phase at an operation temperature, and more preferably is a non-liquid crystal material.

Examples thereof may include:

α -NPD: bis[N-1-(naphthyl)-N-phenyl]benzidine,

1-TANTA: 4,4',4''-tris(1-naphthylphenylamino)-triphenylamine,

2-TANTA: 4,4',4''-tris(2-naphthylphenylamino)-triphenylamine,

TCTA: 4,4',4''-tris(N-carbazoyl)triphenylamine,

p-DPA-TDAB: 1,3,5-tris[N-(4-diphenylaminophenyl)-phenylamino]benzene,

TDAB: 1,3,5-tris(diphenylamino)benzene,

DTATA: 4,4',4''-tris(diphenylamino)triphenylamine,

TDAPB: 1,3,5-tris[(diphenylamino)phenyl]benzene.

[Example]

Example 1

In this example, an organic EL device having a sectional structure as shown in Figure 2 including the conductive liquid crystalline layers having been formed on the ITO electrode on the glass substrate by vacuum deposition was prepared in the following manner. Figure 2 is a schematic sectional view of an organic EL device according to Example 1 of the invention; Figure 2A is a bottom plan view of the organic EL device; Figure 2B is a sectional view taken along a line A-A' of the organic EL device.

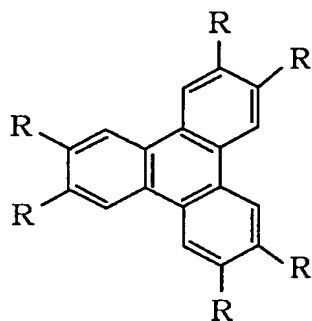
Referring to Figure 2, an organic EL device includes a glass substrate 11 (anode), an ITO layer as an anode electrode for hole injection, a non-aligned liquid crystal region 13 having a low conductivity of the conductive liquid crystalline layer, an aligned liquid crystal region 14 having a higher conductivity of the conductive liquid crystalline layer, a luminescence layer 15 and a cathode electrode 16 disposed in this order on the substrate 11. The conductive liquid crystalline layer has been formed between a pair of oppositely disposed electrodes by vacuum deposition.

More specifically, on a glass substrate 11 held at 200 °C, a 70 nm-thick ITO film was formed as a hole-injecting anode 12 by sputtering using a target

of In 90 wt. % and Sn 10 wt. % while flowing Ar gas at 200 sccm and O₂ gas at 3 sccm. The ITO film showed a work function of ca. 4.35 eV after the sputtering but was then exposed to ultraviolet rays from a low-pressure mercury lamp to have an elevated work function of ca. 4.6 eV.

The above-treated glass substrate 11 having an ITO film 12 was placed in a vacuum chamber held at a pressure below 2.67×10^{-3} Pa (2×10^{-5} torr), and a ca. 35 nm-thick layer of HHOT (hexabis(hexyloxy)-triphenylene) of a formula shown below was formed as a conductive liquid crystal layer 13 on the ITO film 12 by vacuum deposition at a rate of ca. 0.1 nm/sec at a pressure of 1.33×10^{-3} Pa (1×10^{-5} torr) according to the resistance heating vacuum deposition method. HHOT exhibited a mobility of 1×10^{-3} cm²/V.sec at ca. 70 °C or below according to the time-of-flight method. Incidentally, HHOT is a discotic liquid crystal causing a transition from crystal to discotic disordered phase at 65 °C and a transition to isotropic phase at 98 °C.

(Structural formula 1)

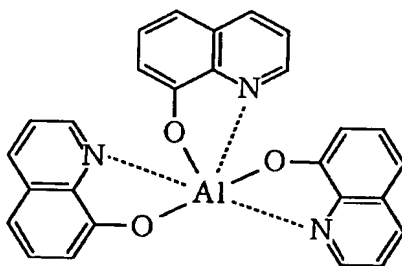


HHOT

R = C₆H₁₃O

Then, on the HHOT layer 13, a luminescence layer 15 of Alq₃ represented by a structural formula shown below was formed in a thickness of 60 nm by vacuum deposition at a rate of ca. 0.1 nm/sec under a pressure of 1.33x10⁻³ Pa (1x10⁻⁵ torr).

(Structural formula 2)



Alq 3

Then, the Alq₃ layer 15 was further coated with a cathode metal 16 comprising a 50 nm-thick layer of Al-Li alloy (Li content = 1.8 wt. %) and a 150 nm thick Al layer, respectively formed by vacuum

deposition, to form a device structure roughly as shown in Figure 2A.

In this state, all the conductive liquid crystalline layers were in an amorphous (non-aligned) state after the conductive liquid crystalline layer including non-aligned liquid crystal regions 13 and aligned liquid crystal regions 14 have been formed by vacuum deposition. In this state, the liquid crystal layer was locally irradiated with CaAlAs laser beam (beam diameter = ca. 20 μ m, 10 mW) and cooled by standing to be provided with locally aligned portions 14 showing a higher conductivity than non-irradiated, non-aligned regions 13.

As a result, on the ITO electrode, HHOT (including non-aligned liquid crystal regions 13 and aligned liquid crystal regions 14), a luminescence layer, and a cathode electrode were disposed in this order, and were formed by vacuum deposition, so that a lamination-type organic EL device having comprising organic layers between the oppositely disposed electrodes was prepared in the following manner. The organic EL device exhibited a display state giving a sufficient contrast in current for flowing the device by voltage application with a predetermined level between the non-aligned liquid crystal regions 13 and the aligned liquid crystal regions 14 of the conductive liquid crystalline layer, so that the

electroluminescence device capable of irradiating by only the aligned liquid crystal regions 14 was obtained. Referring to Figure 2A, the organic EL device comprises a laser-irradiated aligned part 17 and a laser non-irradiated and non-aligned part 18.

Thereafter, the organic EL device was subjected to voltage application under an electric field of 12 volts/100 nm. As a result, the device exhibited luminescence and current with different luminescences at laser-irradiated parts and non-irradiated parts as shown in Table 1 below.

Table 1

	Current (mA/cm ²)	Luminance (cd/m ²)
Laser-irradiated aligned parts	3.593	120
Non-irradiated non-aligned parts	0.05	1.5

(Example 2)

An organic EL device having a sectional structure as shown in Figure 3 including a pixel structure and a conductive liquid crystal layer 53 having a higher conductivity region 53b corresponding to a selected pixel formed by high voltage application

was prepared in the following manner.

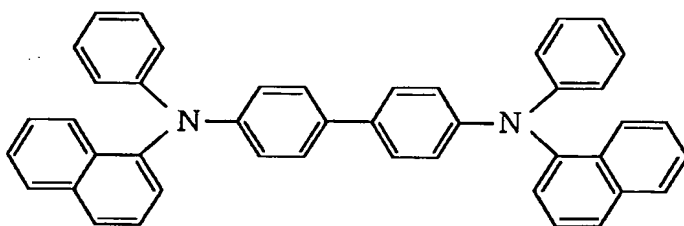
Referring to Figure 3, an organic EL device includes a glass substrate 51 (anode), an ITO layer 52 as an anode electrode for hole injection, a non-aligned liquid crystal region 53 of the conductive liquid crystalline layer, an aligned liquid crystal region 54 of the conductive liquid crystalline layer, a protective layer 55, a luminescence layer 56 and a cathode electrode 57 disposed in this order on the glass substrate 11. The conductive liquid crystalline layers 53 and 54 have been formed between a pair of opposing electrodes by vacuum deposition.

More specifically, on a glass substrate 51 held at 200 °C, a 70 nm-thick ITO film 52 was formed as a hole-injecting anode by sputtering using a target of In 90 wt. % and Sn 10 wt. % while flowing Ar gas at 200 sccm and O₂ gas at 3 sccm. The ITO film 52 shows a work function of ca. 4.35 eV after the sputtering but was then exposed to ultraviolet rays from a low-pressure mercury lamp to have an elevated work function of ca. 4.6 eV.

The above-treated glass substrate 51 having an ITO film 52 was placed in a vacuum chamber held at a pressure below 2.67×10^{-3} pa (2×10^{-5} torr), and a ca. 35 nm-thick layer of HHOT (hexabis(hexyloxy)-triphenylene) of a formula shown below was formed as a conductive liquid crystal layers 53 and 54 on the ITO

film 52 by vacuum deposition at a rate of ca. 0.1 nm/sec at a pressure of 1.33×10^{-3} Pa (1×10^{-5} torr) according to the resistance heating vacuum deposition method. HHOT exhibited a mobility of 1×10^{-3} cm²/v.sec at ca. 70 °C or below according to the time-of-flight method. Incidentally, HHOT is a discotic liquid crystal causing a transition from crystal to discotic disordered phase at 65 °C and a transition to isotropic phase at 98 °C.

Then, between the luminescence layer 56 and the conductive liquid crystal layers 53 and 54, a-NPD layer (as a protective layer) represented by a structural formula shown below was formed in thickness of 60 nm by vacuum deposition at a rate of ca. 0.1 nm/sec under a pressure of 1.33×10^{-3} Pa (1×10^{-5} torr). (Structural formula 3)

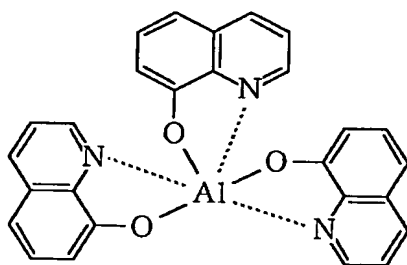


α NPD

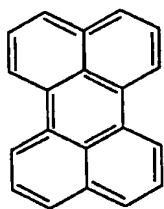
Luminescence organic layer segments 56 exhibiting different luminescent wavelengths were respectively formed in a thickness of 50 nm on the protective layer 54 by vacuum deposition through a mask under the conditions of a pressure of 1×10^{-5} torr

and a deposition rate of ca. 0.1 nm/sec. The organic layers 55a - 55c were respectively formed of Alq3 represented by a structural formula 2 shown alone, Alq3 doped with 5 wt. % of perylene for shifting the luminescence wavelength to a shorter wavelength side, and Alq3 doped with 5 wt. % of DCM (a styryl dye) for shifting to a longer wavelength side. The structural formulae for the above-mentioned perylene and DCM are shown below.

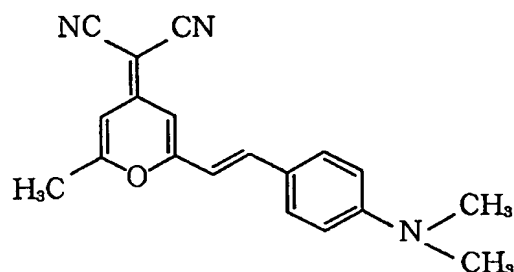
(Structural formula 4)



Alq 3



perylene



DCM

The above-prepared organic layers 56 were respectively coated with cathode metals 57 each comprising a 50 nm-thick layer of Al-Li alloy (Li content = 1.8 wt. %) and a 150 nm-thick Al layer, respectively formed by vacuum deposition, to obtain an organic EL device having a structure as shown in Figure 3.

On the ITO electrode, a HHOT (including non-aligned liquid crystal regions 13 and aligned liquid crystal regions 14), a luminescence layer, and a cathode electrode were disposed in this order, and were formed by vacuum deposition, so that an organic EL device having the organic layers with the multi-layers structure was prepared, the above-prepared device was confirmed to exhibit luminescence at an increased luminance at an increased current when maintained at 75 °C.

In this example, only a selected pixel portion of the organic layers including a luminescence segment (55a in Figure 3) was supplied with a high

electric field of 15 volts/100 nm for 3 min. at 30 °C, and the other segments (55b and 55c in Figure 3) were not subjected to the high voltage application treatment. Thereafter, all the segments 55a - 55c were supplied with a drive electric field of 5 volts/100 nm at 30 °C. As a result, the segment 55c subjected to the high-voltage application treatment exhibited a selectively high luminance as shown in Table 2 below.

Table 2

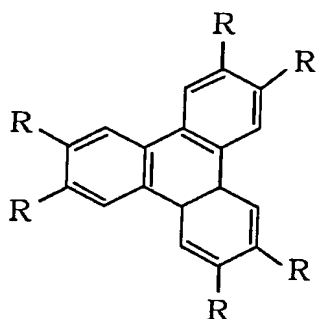
	Current (mA/cm ²)	Luminance (cd/m ²)
High voltage treatment applied (55a, 53b)	12	300
High voltage treatment not applied (55b-55c, 53a)	<0.05	0

Example 3

In this example, an organic EL device having a sectional structure as shown in Figure 3 was prepared in the same manner as in Example 2 except for using HPOT (hexabis(pentyloxy)triphenylene) having a disordered phase of a discotic liquid crystal

material, of a structural formula shown below was used instead of HHOT for providing a conductive liquid crystal layer and except that the liquid crystal layer was locally irradiated with GaAlAs laser beam (beam diameter = ca. 20 μ m, 10 mW) and cooled by standing to be provided with locally aligned portions 14 showing a higher conductivity of the conductive liquid crystalline layer.

(Structural formula 5)



HPOT R = C₆H₁₁O

As a result, on the ITO electrode, HHOT (including non-aligned liquid crystal layer 53 and aligned liquid crystal layer 54), a luminescence layer, and a cathode electrode were disposed in this order, and were formed by vacuum deposition, so that a lamination-type organic EL device comprising the organic layers between the oppositely disposed electrodes was prepared in the following manner. The organic EL device exhibited a display state giving a sufficient contrast in current for flowing the device by voltage application with a predetermined level

between the non-aligned liquid crystal regions 53 and the aligned liquid crystal regions 54 of the conductive liquid crystalline layer, so that the electroluminescence device capable of irradiating by only the aligned liquid crystal regions 54 was obtained.

Thereafter, the organic EL device was subjected to voltage application under an electric field of 12 volts/100 nm. As a result, the device exhibited luminescence and current with different luminescences at laser-irradiated parts and non-irradiated parts as shown in Table 3 below.

Table 3

	Current (mA/cm ²)	Luminance (cd/m ²)
Laser-irradiated aligned parts (55a, 53b)	11.5	500
Non-irradiated non-aligned parts (55b-55c, 53a)	2.3	90

Therefore, the organic EL device was subjected to voltage application under an electric field of 10 volts/100 nm. As a result, the device exhibited luminescence and current with different

luminescences at laser-irradiated parts and non-irradiated parts as shown in Table 4 below.

Table 4

	Current (mA/cm ²)	Luminance (cd/m ²)
Laser-irradiated aligned parts (55a, 53b)	3.0	110
Non-irradiated non-aligned parts (55b-55c, 53a)	0.4	18

[Advantageous Effect]

As described above, according to the present invention, it has become possible to provide an organic EL device having a memory characteristic by including a conductive liquid crystal layer having regions of different conductivities on the electrode. Compared with a conventional EL device lacking a recordability (memory characteristic) of written or display state, the EL device of the present invention can exhibit locally different luminances at an identical drive voltage. This characteristic is available not only in a display device, but also in a memory device.

[Brief Description of the Drawings]

Figure 1 is a schematic sectional view of an embodiment of a conductive liquid crystal device according to the invention.

Figure 2A is a schematic sectional view of an organic EL device according to Example 1 of the invention, and Figure 2B is a corresponding bottom plan view.

Figure 3 is a schematic sectional view of an organic EL device according to Example 2 of the invention.

[Reference Numerals]

- 1: transparent substrate
- 2: transparent electrode (anode)
- 3: liquid crystalline organic layer
- 5: luminescence layer
- 5a: non-aligned liquid crystal region
- 5b: aligned liquid crystal region
- 6: metal electrode (cathode)
- 11: glass substrate
- 12: ITO film
- 13: non-aligned liquid crystal region
- 14: aligned liquid crystal region
- 15: luminescence layer
- 16: cathode electrode
- 17: irradiated luminescent part
- 18: non-irradiated non-luminescent part

- 51: glass substrate
- 52: ITO layer
- 53: non-aligned conductive liquid crystalline
layer
- 54: aligned conductive liquid crystalline layer
- 55: protection layer
- 56: luminescence layer
- 57: cathode electrode

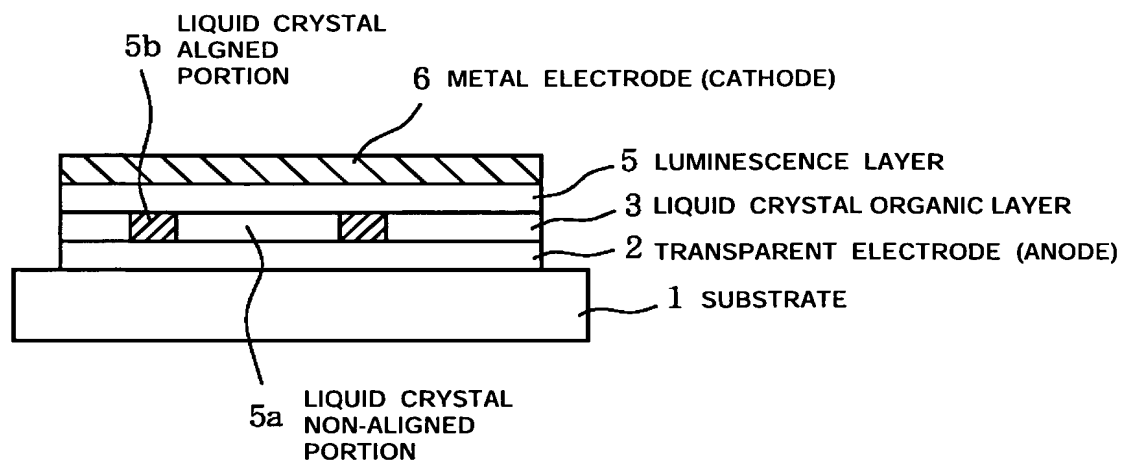


FIG. 1

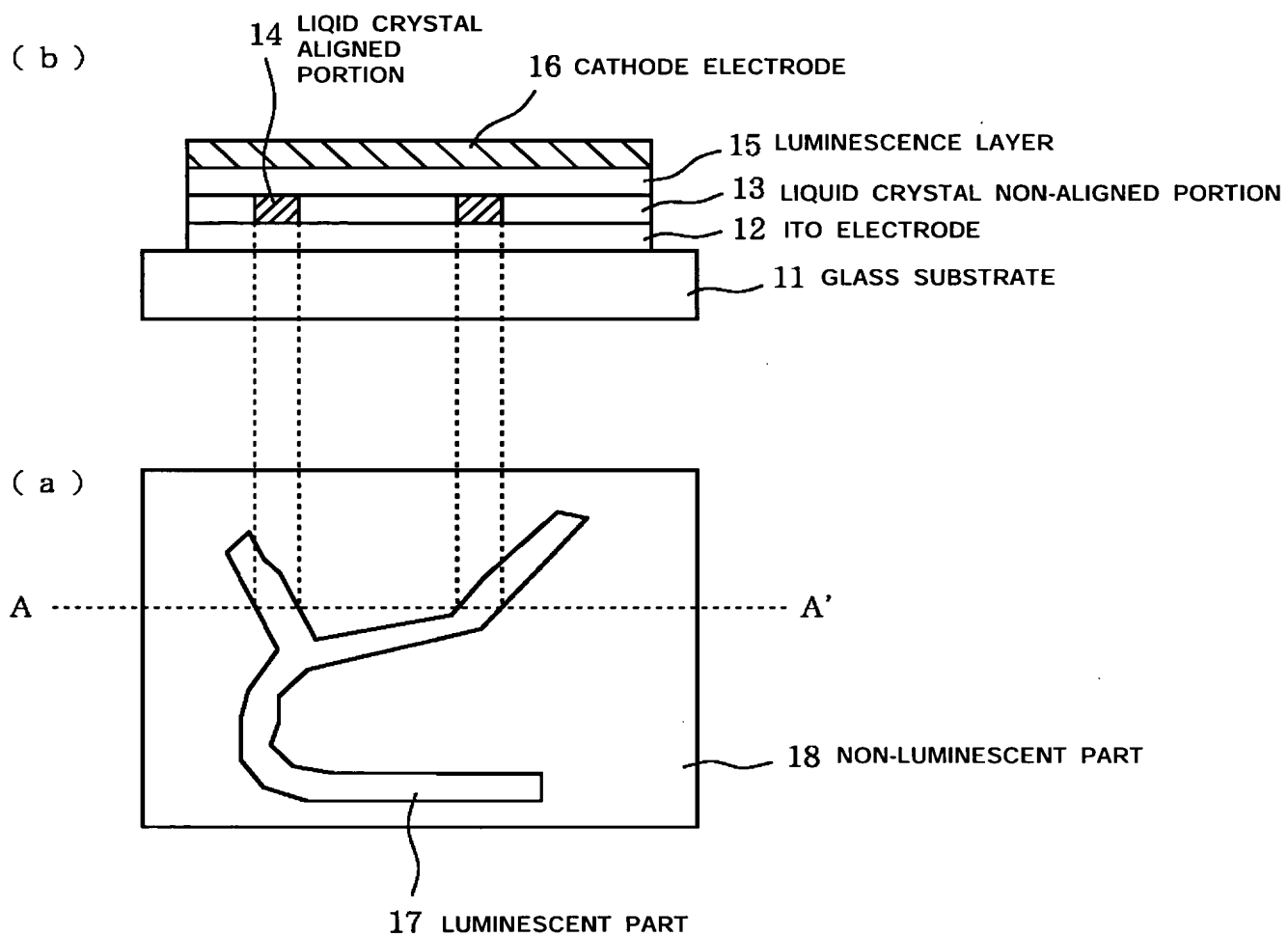


FIG. 2

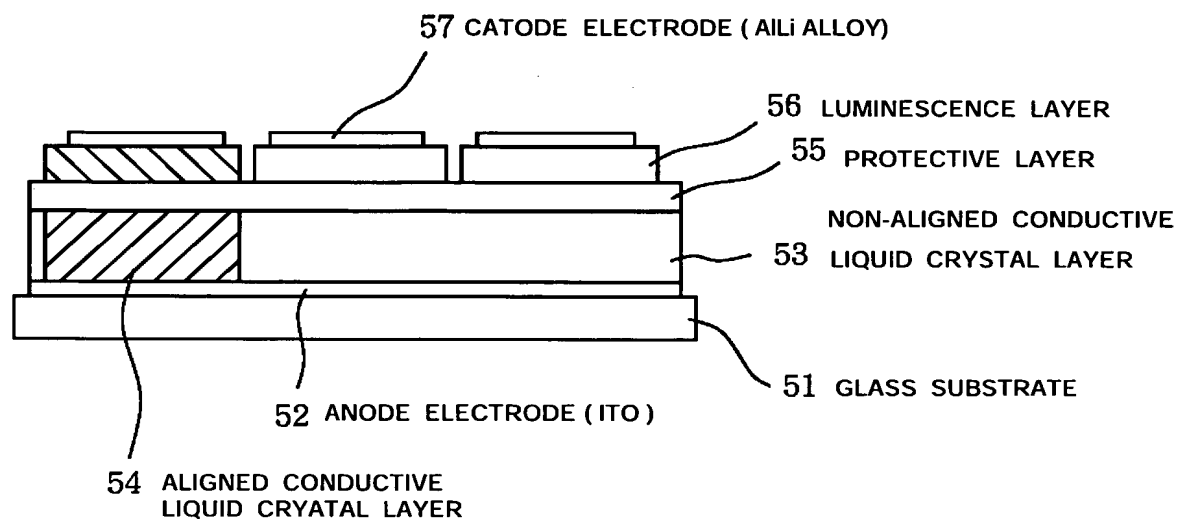


FIG. 3

[Document]

Abstract

[Abstract]

[Object]

It is a principal object of the present invention to provide a conductive liquid crystal device having a memory characteristic which can exhibit locally different luminescences at an identical drive voltage.

[Means for Solving]

There is provided a conductive liquid crystal which comprises a substrate 1, a transparent electrode (anode) 2, a liquid crystalline organic layer 3, a luminescence layer 5 and a metal electrode (cathode) 6 disposed in this order on the transparent electrode 2, wherein the liquid crystalline organic layer 3 is provided with plural regions having mutually different electroconductivities including non-aligned liquid crystal regions 5a having a lower conductivity and aligned liquid crystal regions 5b having a higher conductivity.

[Selected Figure]

Figure 1